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Squaraines based on 2-arylpyrroles

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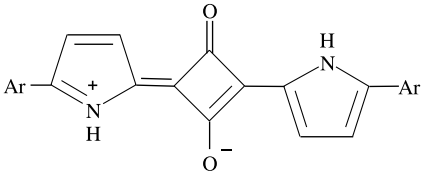
Abstract—Various derivatives of 2-phenylpyrrole were condensed with squaric acid to give the corresponding squaraines. The products are drawn with the *anti* geometry rather than the *syn* geometry generally shown in the past: the arguments for this formulation are given, including the analogy with 2,5-bis(4-ethyl-3,5-dimethylpyrrol-2-yl)-1,4-benzoquinone, for which an X-ray structure is presented. Solutions of the new bis(5-arylpyrrol-2-yl)squaraines have intense, sharp absorption bands shifted to the red. Condensation of squaric acid with arylpyrroles possessing fused ring systems, and condensation with 2-styrylpyrrole, gave chromophores with high values for λ_{max} and ε_{max}. Certain of these chromophores appear to be suitable for further structural elaboration to give materials having potential in optoelectronic and photodynamic applications.

1. Introduction

The squaraines are a series of organic dyestuffs characterised by intense absorption in the red region of the spectrum. They have attracted considerable commercial interest because of their optoelectronic properties, finding applications in such areas as solar cells, xerographic sensitisers, near-IR dyes and optical recording.[1–4] There has also been some limited activity in applications as sensitisers in photodynamic therapy.[5–9] In both of these areas, two current interests are (i) to shift the absorption maximum to lower energies, and (ii) to alter the solution properties, since many of the squaraines have poor solubility in polar and in non-polar solvents. Here we address the first of these.

Our present aim has been to investigate the preparation and electronic absorption spectra of 2,4-bis(5-arylpyrrol-2-yl)squaraines **1**. Such molecules might be advantageous here since they would be expected to have red-shifted absorption maxima (with respect to the parent skeleton) because of the aryl conjugation; and the aryl ring would provide sites for substituents aimed at modulating solution and spectroscopic properties.

Although the bis(pyrrol-2-yl)squaraines were amongst the first of the squaraine dyes to be reported,[10,11] they have subsequently been relatively little studied, and the 5-arylpyrrol-2-yl derivatives are unknown. The photophysical properties of bis(4-acetyl-3,5-dimethylpyrrol-2-yl)-squaraine have been reported.[12] Recently there have been several reports on the non-linear optical properties,[13,14] electrical conductivities,[15–18] and lithium ion sequestration[19] of various polymeric (*N*-alkylpyrrol-2-yl)squaraines. Copolymers comprised of bis(pyrrol-2-yl)squaraine units based on *N*-substituted and *N*-unsubstituted pyrroles have also been prepared.[20]



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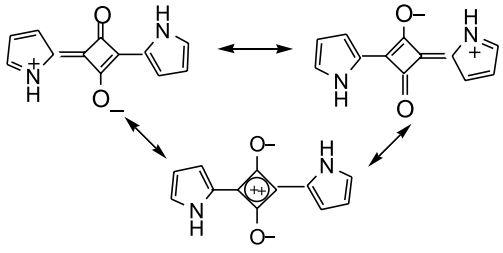
Ar = Ph, substituted Ph, naphthyl, etc

The bis-pyrrolylsquaraines are highly π-delocalised systems which may be regarded as possessing 2πe aromaticity, as shown in Scheme 1. Thus the carbonyl stretching



Scheme 1. Delocalisation in the bis(pyrrol-2-yl)squaraine system.

Keywords: Oxocarbon acids and derivatives; Electronic spectra; Pyrroles, Aryl; Red-absorbing dyes.
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frequency in the IR spectrum appears at about 1600 cm^{-1}, consistent with considerable single bond character.

For the various applications already mentioned, the squaraines have some distinct advantages, especially the sharp intense absorption in the red region. Thus the squaraine **2** has λ_{max} 560 nm (ε 200,000 M^{-1} cm^{-1}) in chloroform (Fig. 1) which is little affected by modest changes in the acidity of the medium (small hypsochromic shift in $CHCl_3$–HCl). Secondly, such compounds can be synthesised, usually in good yield, in one step from squaric acid and an α-free pyrrole. Thus in the original work of Treibs and Jacob[10,11] compound **2** was obtained in 90% isolated yield from kryptopyrrole as shown in Scheme 2. Such a one step preparation is a clear benefit with respect to cost and environmental considerations when a potentially commercial interest is in view, although the starting materials still have to be obtained. Thirdly, although most squaraines that have been described have symmetrical structures, it is possible to carry out the synthesis in two independent stages, and so attach two different π-excessive units, thus increasing the range of structural variation.[4,21–23]

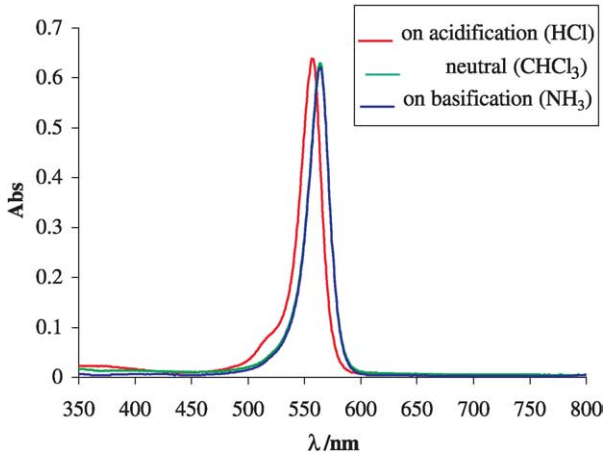
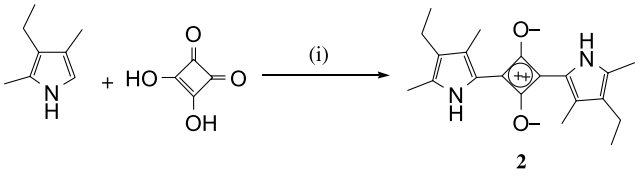


Figure 1. The electronic absorption spectrum of 2,4-bis(4-ethyl-3,5-dimethylpyrrol-2-yl)cyclobutenediylium-1,3-diolate [2,4-bis(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine] **2** in chloroform.

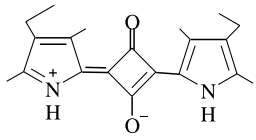


Scheme 2. Synthesis of 2,4-bis(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine **2**. (i) *n*-BuOH/PhH = 1:1, reflux, 3 h.

2. Results and discussion

2.1. Structure

It is necessary at the outset to address the question of the detailed structure of 2,4-bis(pyrrol-2-yl)squaraine [2,4-bis(pyrrol-2-yl)cyclobutenediylium-1,3-diolate]. When Treibs and Jacob first described **2**, the structure was drawn as shown at **3**, and the majority of subsequent authors of original papers and reviews have followed suit:[3,12,24] reference 25, where an *anti* structure is given without specific comment, appears to be the only exception. The matter has been given some attention for squaraines derived from *N*-substituted pyrroles. Thus the squaraine obtained from 2,4-dimethyl-1-octadecylpyrrole behaves as a single substance, and has been thought most likely to prefer the *anti* geometry **4** for steric reasons.[13] Polymeric systems derived from *N*-alkylpyrroles have also sometimes been represented with the *anti* stereochemistry.[19,26]



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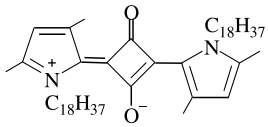

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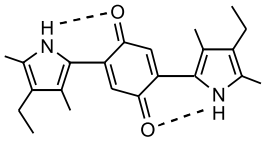
We believe that for the squaraines derived from *N*-unsubstituted pyrroles the *anti* stereochemistry shown in Scheme 1 will be preferred because it maximises intramolecular hydrogen bonding. Such intramolecular hydrogen bonding involving pyrrolic imino hydrogen has been encountered elsewhere, for example in bilirubin (where it is also thought to be associated with low solubility in polar solvents).[27]

Attempts to grow crystals of the new bis(2-arylpyrrol-2-yl)squaraines (below) suitable for X-ray analysis have not so far been successful, and we have found no closely related X-ray structure in the literature. However, we have carried out a crystal analysis of a structurally related compound, the 2,5-bis(pyrrol-2-yl)-1,4-benzoquinone **5**,[28] which is found to have the intramolecularly hydrogen bonded structure shown in Figure 2. Moreover, the observed bond lengths accord with contributions from canonicals such as **6**, again analogous to the situation shown in Scheme 1.



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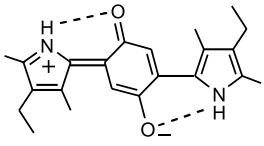

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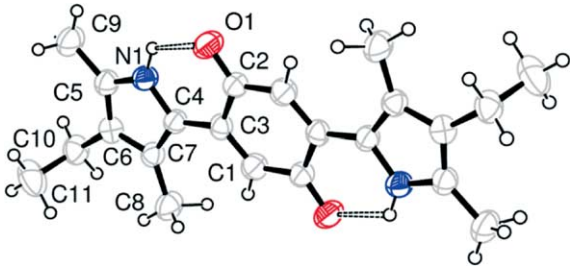


Figure 2. Molecular structure of 2,5-bis(4-ethyl-3,5-dimethylpyrrol-2-yl)-1,4-benzoquinone [2,5-bis(4-ethyl-3,5-dimethylpyrrol-2-yl)cyclohexadiene-1,4-dione] **5** (crystallographic numbering shown).

Thus, in **5** the C–O bond lengths are 1.242 Å (1.222 Å in 1,4-benzoquinone)[29] indicating increased single bond character, confirmed by the IR stretching frequency at 1602 cm^{-1}. These and other bond lengths selected for their relevance to this point are shown in Figure 3. Particularly

significant are the lengthening in the six membered ring of the C1–C2 and C2–C3 bonds, and the shortening of the C3–C4 bond (chemical numbering) with respect to the corresponding values in 1,4-benzoquinone.

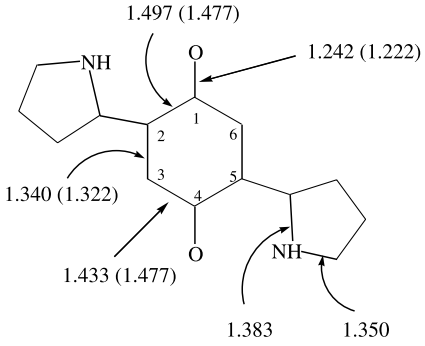


Figure 3. Selected bond lengths (Å) of compound **5** compared with corresponding bond lengths in 1,4-benzoquinone (in parenthesis).[29,30] (Chemical numbering shown).

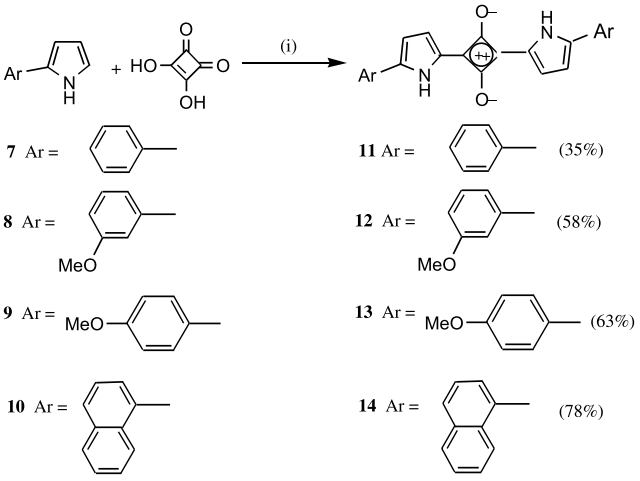
Thus in this paper we show the bispyrrol-2-ylsquaraines with the *anti* geometry (as in Scheme 1) throughout. This is not to imply that the alternative geometry may not be accessible in solution by overcoming the barrier to restricted rotation. Although ^{1}H NMR work has not led to its detection with the new compounds described here, such equilibration has been observed in this way with other systems (e.g. with dialkylaminohydroxyphenyl squaraines).[25] Recent studies in non-protic solvents on semisquaraines with *o*-diethylaminophenyl substitution have been interpreted in terms of intramolecular hydrogen bonding which is disrupted in protic solvents.[31]

2.2. 2,4-Bis(5-arylpyrrol-2-yl)squaraines

Our approach has thus been to push the absorption maximum of the bis-pyrrolylsquaraine system towards the red by introducing α-aryl substituents and by constraining such substituents more or less to the plane by non-conjugative ring formation. Such an approach has been used recently in modifying the chromophores of difluoroboron(III) pyrromethene derivatives used as fluorescent labels for DNA sequencing to increase the range of absorption and fluorescence.[32,33]

2-Phenylpyrrole **7** and its derivatives **8**–**10** were prepared by coupling *N*-Boc-2-bromopyrrole[34] with the appropriate arylboronic acid using the Suzuki reaction.[33] Condensation of these 2-arylpyrroles **7**–**10** with squaric acid in butanol–benzene in the presence of molecular sieve gave the corresponding squaraines **11**–**14** (Scheme 3) as crystalline or amorphous greenish solids. The squaraines were characterised by elemental analysis and/or HRMS and by spectroscopic methods.

Some minor problems were encountered: the crystals tended to retain water (observed also by others[11]): and in some cases it was not possible to obtain satisfactory ^{1}H NMR spectra, which is attributed to low solubility and/or to line broadening by radical impurities. The electronic spectra of compounds **11**–**14** are compared graphically in Figure 4, and refer to chloroform solution: treatment with traces of acid and base (cf. Fig. 1) caused little or no discernible change (data not shown).



Scheme 3. Condensation of squaric acid with 2-phenylpyrrole and analogues to give the corresponding squaraines. [(i)=*n*-BuOH–benzene, △, 4 h, molecular sieves].

It is apparent that the introduction of the 2-phenyl substituent into the pyrrole moiety causes a marked bathochromic shift (λ_{max} 564 nm for **2**, 621 nm for **11**). The peak is further shifted to lower energy by the *p*-methoxy group in **13** (λ_{max} 643 nm, cf. delocalisation pathway in **15**) but is essentially unaffected by the *m*-methoxy group in **12** (λ_{max} 624 nm, oxygen lone pair not delocalisable onto the squaraine system), except that the molecular absorbance decreases. The absorption bands are particularly sharp, with little absorption in the remaining part of the visible region, and the solutions are strikingly coloured (purple-blue shades) the brilliance of which we suppose to be associated with the narrowness of this absorption band.

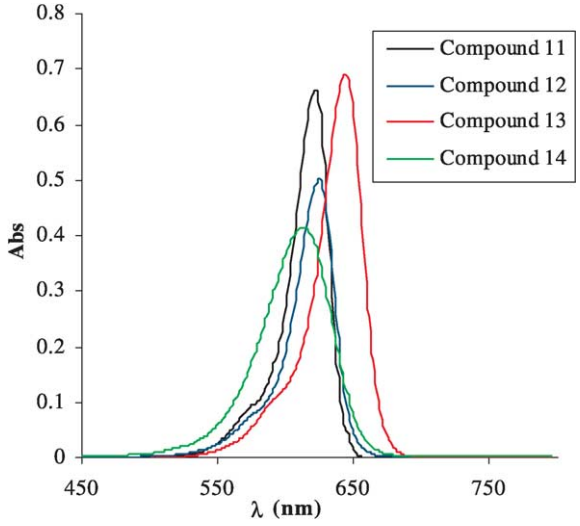
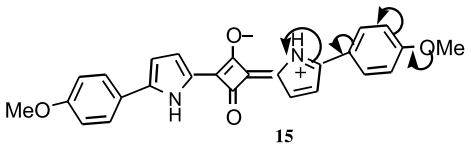
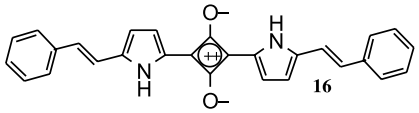


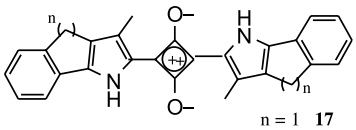
Figure 4. The electronic absorption spectra of squaraines **11**–**14** in chloroform.



However, the spectrum of the α-(1-naphthyl) derivative **14** showed quite different behaviour: the λ_{max} value had decreased (613 nm) and the peak had become broader and less intense (Fig. 4). This is attributed to a steric effect which causes the larger naphthyl substituent to rotate out-of-plane, leading to reduced conjugation.

The example of the α-(1-naphthyl) derivative **14** pointed to the need to facilitate conjugation by introducing features which enhance coplanarity of the benzenoid and squaraine chromophores. We sought to do this in two ways: (i) by using styryl rather than phenyl substitution, as in **16**; and (ii) by introducing an additional saturated ring to force the benzenoid substituent to lie more or less in the plane of the bispyrrolylsquaraine nucleus, as in **17** and **18**.





2-(*E*)-Styrylpyrrole **19**[35] was condensed with squaric acid as before to give 2,4-bis[5-(*E*)-styrylpyrrol-2-yl]cyclobutenediylium-1,3-diolate **16** as a dark green solid in 54% yield. The electronic spectrum in chloroform (Fig. 5) showed λ_{max} 673 nm (ε 146,000 M^{-1} cm^{-1}). Although the molecular absorbance is lower than might have been expected, the λ_{max} of the absorption band is shifted well into the red. Since this work was completed, a tetramethoxy derivative of 2,4-bis[5-(*E*)-styrylpyrrol-2-yl]squaraine has been reported to have λ_{max} 695 nm, showing the pronounced auxochromic effect of additional methoxy groups.[3]

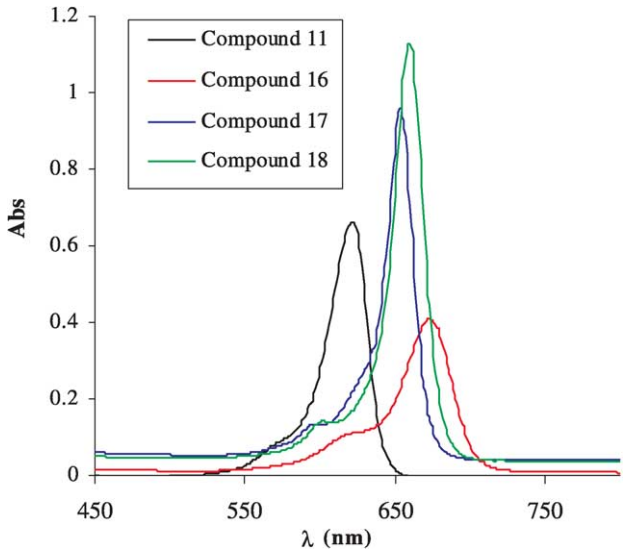
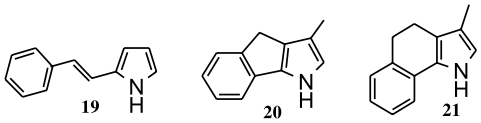


Figure 5. The electronic absorption spectra of squaraine compounds **11** and **16**–**18** in chloroform. The base line for **17** and **18** has been displaced for clarity.



3-Methyl-4*H*-indano[1,2-*b*]pyrrole **20**[32] was condensed with squaric acid to give the corresponding squaraine **17** as fine lustrous greenish needles in 42% yield. This substance was especially difficult to study because of its poor solubility: it was sparingly soluble in pyridine and in trifluoroacetic acid, which proved to be satisfactory solvents for several of the squaraines studied here. Squaraine **17** gave a satisfactory analysis, but it was not sufficiently soluble (DTFA–$CDCl_3$; pyridine-d_5) to give a ^1H NMR spectrum. The electronic spectrum (chloroform) is shown in Figure 5 (λ_{max} 654 nm, ε 347,000 M^{-1} cm^{-1}). In an analogous manner, 3-methyl-4,5-dihydro-1*H*-benz[1,2-*g*]indole **21**[32] condensed with squaric acid to give the squaraine **18** as fine green needles in 80% yield. It gave satisfactory elemental analysis and high resolution molecular ion measurements. Although in this case the substance did dissolve in pyridine–chloroform to give a bright green solution, a satisfactory ^1H NMR spectrum was not obtained. The electronic spectrum showed a sharp band at 660 nm with a high ε value (403,500 M^{-1} cm^{-1}).

Thus with respect to the 2-phenylpyrrole squaraine derivative **11**, both structural variations, i.e. the extended conjugation in **16**, and the constraints imposed in **17** and **18**, have led to significant shifts of the absorption band into the red region, with the additional advantage of marked hyperchromic effects for **17** and **18**.

3. Conclusions

(i) It is argued that the preferred geometry of the *N*-unsubstituted bis(pyrrol-2-yl)squaraine system is *anti* because this geometry allows greater intramolecular hydrogen bonding than the *syn* structure. This conclusion is supported by an X-ray crystal structure of a closely analogous compound, 2,5-bis(4-ethyl-3,5-dimethylpyrrol-2-yl)-1,4-benzoquinone **5**.

(ii) Squaraines derived from 2-arylpyrroles are prepared for the first time. They possess sharp strong absorption bands shifted to the red region of the spectrum when compared with the known alkylated analogues. Especially is this so for the molecules in which the aryl ring is constrained to be more or less in the plane of the pyrrole ring, as in **18** (λ_{max} 660 nm, ε 403,500 M^{-1} cm^{-1}).

(iii) The chromophores represented by **13**, **16**, **17** and **18** may have potential for optoelectronic and photodynamic therapeutical applications. Solubility in common solvents remains a problem with the present compounds, but the presence within these structures of benzenoid sites which can carry groups designed to modulate physical properties (particularly solubility

and photophysical parameters) offers a pathway for future development.

4. Experimental

4.1. General

Electronic spectra were measured on a Perkin–Elmer 552 spectrometer; ^{1}H NMR spectra were measured with tetramethylsilane as internal standard and were recorded either with a Brüker AM-250, a JEOL EX-270, a Brüker AMX-400 or a Brüker AMX-600 (ULIRS service) instrument. The coupling constants (J values) are given in Hz; peak assignments for **12–14** by COSY and NOESY spectroscopy. Mass spectra were recorded on a Micromass ZAB-2SE (ULIRS service): relative abundances and assignments are given in parentheses. Unless otherwise stated ionisation was by fast atomic bombardment (FAB): the matrix was *m*-nitrobenzyl alcohol (NOBA). Mps were measured on a hot-stage apparatus, and are uncorrected. Reactions were monitored using TLC on Merck Kieselgel 60 silica gel plastic sheets. Column chromatography was carried out on Merck Kieselgel 60 silica gel (0.040–0.063 mm). The 2-aryl pyrroles **7–10** were prepared by coupling *N*-*t*-butyloxycarbonyl-2-bromopyrrole with the appropriate arylboronic acid as described in the literature.[33]

4.2. General procedure for the synthesis of squaraine derivatives

4.2.1. 2,4-Bis[5-phenylpyrrol-2-yl]cyclobutenediylium-1,3-diolate (11). 2-Phenylpyrrole **7** (35 mg, 0.24 mmol), and squaric acid (11.5 mg, 0.10 mmol) were dissolved in butanol/benzene (1:1) (10 mL) and refluxed for 4 h with 4 Å molecular sieves (ca. 50 mg). The reaction mixture was cooled to room temperature; ethanol (4 mL) was added and the mixture was decanted from the molecular sieves and kept in the freezer overnight. The crystalline product was filtered off, washed with ethanol (20 mL), and dried to give the title squaraine (12.9 mg, 35%) as lustrous greenish needles, mp $>$ 300 °C; R_f=0.40 (EtOAc:CHCl$_3$=3:7). This substance did not give satisfactory NMR signals in DMSO-d_6, DTFA–CDCl$_3$, and pyridine-d_5, due to poor solubility. λ_{max} (CHCl$_3$)/nm 621 (ε 237,000 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3400, 1618, 1583, 1560, 945, 918, 758; *m*/*z* (FAB) 365 (100, M+H), 364 (50, M), 363 (35), 199 (75); HRMS M+H, $C_{24}H_{17}N_2O_2$ calcd 365.1290, found 365.1285. Anal. calcd for $C_{24}H_{16}N_2O_2\cdot 1.8H_2O$, C, 72.64; H, 4.98; N, 7.06. Found C, 72.53; H, 4.34; N, 6.82.

4.2.2. 2,4-Bis[5-(3-methoxy)phenylpyrrol-2-yl]cyclobutenediylium-1,3-diolate (12). Lustrous greenish needles (58%), mp $>$ 300 °C; R_f=0.35 (EtOAc/CHCl$_3$ =3:7); δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 7.73 (2H, bd, pyrrole 3-H), 7.46 (4H, m, benzenoid C5′ and C6′), 7.38 (2H, bs, benzenoid C2′), 7.10 (2H, m, benzenoid C4′), 7.06 (2H, d, J=4.8 Hz, 4-H of pyrrole), 4.00 (6H, s, OMe). λ_{max} (CHCl$_3$)/nm 625 (ε 177,000 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3393, 1635, 1603, 1558, 1508, 934, 822, 800; *m*/*z* (FAB) 425 (100, M+H), 346 (35); HRMS M+H, $C_{26}H_{21}N_2O_4$ calcd 425.1501, found 425.1516. Anal. calcd for $C_{26}H_{20}N_2O_4\cdot 0.5H_2O$, C, 72.04; H, 4.88; N, 6.46. Found C, 72.07; H, 4.78; N, 6.21.

4.2.3. 2,4-Bis[5-(4-methoxyphenyl)pyrrol-2-yl]cyclobutenediylium-1,3-diolate (13). Lustrous greenish crystals (63%), mp 230 °C; δ_H (400 MHz; d$_5$-pyridine–CDCl$_3$; Me$_4$Si) 7.99 (4H, d, J=8.8 Hz, AA′BB′ benzenoid C2′ and C6′ H), 7.95 (2H, d, J=3.8 Hz, 3-H of pyrrole), 7.02 (2H, d, J=3.8 Hz, 4-H of pyrrole), 6.94 (4H, d, J=8.8 Hz, AA′BB′ benzenoid C3′ and C5′ H), 3.70 (6H, s, OMe). λ_{max} (CHCl$_3$)/nm 643 (ε 248,000 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3393, 1603, 1583, 1560, 941, 916, 829, 797, 783; *m*/*z* (FAB) 425 (35, M+H), 424 (35, M), 336 (55); HRMS M+H, $C_{26}H_{21}N_2O_4$ calcd 425.1501, found 425.1516. Anal. calcd for $C_{26}H_{20}N_2O_4\cdot 0.1H_2O$ requires C, 73.26; H, 4.78; N, 6.57. Found C, 73.19; H, 4.83; N, 6.34.

4.2.4. 2,4-Bis[5-(1-naphthyl)pyrrol-2-yl]cyclobutenediylium-1,3-diolate (14). Greenish solid (78%), mp $>$ 300 °C; R_f=0.36 (EtOAc/CHCl$_3$=3:7); δ_H (400 MHz; DTFA–CDCl$_3$; Me$_4$Si) 8.20 (2H, m, naphthyl C-1′H), 8.05, 7.95 (each 2H, m, naphthyl C–H), 7.82 (2H, m, 3-H of pyrrole), 7.70 (2H, bs, naphthyl C–H), 7.61 (6H, m, naphthyl C-3′, 6′ and 7′ H), 7.15 (2H, m, 4-H of pyrrole). λ_{max} (CHCl$_3$)/nm 613 (ε 149,000 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3425, 3051, 1624, 1593, 1558, 1516, 945, 768 and 664; *m*/*z* (FAB) 487 (13, M+Na), 465 (90, M+H), 464 (100, M), 443 (25), 349 (33), 336 (57), 329 (87), 307 (48), 289 (40), 264 (28); HRMS M, $C_{32}H_{20}N_2O_2$ calcd 464.1525, found 464.1502. Anal. calcd for $C_{32}H_{20}N_2O_2$, C, 82.74; H, 4.34; N, 6.03. Found C, 81.91; H, 4.29; N, 5.75.

4.2.5. 2,4-Bis[(*E*)-5-styrylpyrrol-2-yl]cyclobutenediylium-1,3-diolate (16). Greenish solid (54%), mp $>$ 300 °C; R_f=0.40 (EtOAc/CHCl$_3$=3:7). This substance did not give a satisfactory ^{1}H NMR spectrum in CDCl$_3$/DTFA or in pyridine-d_5. λ_{max} (CHCl$_3$)/nm 673 (ε 146,000 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3421, 1593, 1551, 1501, 941, 847, 799, 745, 687 and 640; *m*/*z* (FAB) 417 (78, M+H), 416 (82, M), 338 (45); HRMS M, $C_{28}H_{20}N_2O_2$ calcd 416.1525, found 416.1505.

4.2.6. 2,4-Bis[5-(4-methyl)indano-4*H*-[1,2-*b*]pyrrol-2-yl]cyclobutenediylium-1,3-diolate (17). Lustrous greenish fine needles (42%), mp $>$ 300 °C. An ^{1}H NMR spectrum could not be obtained (low solubility in CDCl$_3$/DTFA and pyridine-d_5). λ_{max} (CHCl$_3$)/nm 654 (ε 347,000 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3450, 1612, 1535, 1447, 1408, 1045, 945, 814, 795, 768 and 714; *m*/*z* (FAB); HRMS M, $C_{28}H_{20}N_2O_2$ calcd 416.1525, found 416.1545. Anal. calcd for $C_{28}H_{20}N_2O_2$, C, 80.75; H, 4.84; N, 6.73. Found C, 80.92; H, 4.90; N, 6.49.

4.2.7. 2,4-Bis[5-(3-methyl-4,5-dihydro-1*H*)benz[*g*]-indolyl-2-yl]cyclobutenediylium-1,3-diolate (18). Fine greenish crystals (80%), mp 280 °C; R_f=0.72 (EtOAc/CHCl$_3$=3:7). ^{1}H NMR spectra could not be obtained (low solubility in CDCl$_3$/DTFA and pyridine-d_5). λ_{max} (CHCl$_3$)/nm 660 (ε 403,500 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3400, 1612, 1528, 1472, 1420, 1369, 1302, 1283, 1180, 1113, 1088, 1061, 972, 955, 885 and 764; *m*/*z* (FAB) 445 (33, M+H), 444 (50, M), 329 (40); HRMS M, $C_{30}H_{24}N_2O_2$ calcd 444.1838, found 444.1846. Anal. calcd for $C_{30}H_{24}N_2O_2$, C, 81.05; H, 5.44; N, 6.30. Found C, 81.25; H, 5.44; N, 6.27.

4.3. Model compound

4.3.1. 2,5-Bis[3,5-dimethyl-4-ethylpyrrol-2-yl]cyclohexadiene-1,4-dione (5). 3-Ethyl-2,4-dimethylpyrrole (30 mg, 0.24 mmol) in ethanol (3 ml) and 1,4-benzoquinone (36.3 mg, 0.34 mmol.) in chloroform/ethanol mixture (1:1) (3 ml) were mixed together and stirred at room temperature for 20 min. The solution became purple in colour, and then very dark. The reaction was diluted with ethanol (6 ml) and kept in the freezer overnight. The greenish purple solid was filtered off and washed with ethanol (10 ml) to give 12 mg (28% yield) of the title quinone as a dark purple solid with a greenish iridescence, mp 245–250 °C (lit[28] mp 250 °C); R_f=0.33 (light petroleum/$CHCl_3$ =1:4); δ_H (400 MHz; $CDCl_3$; Me_4Si) 10.90 (2H, bs, N–H), 6.60 (2H, s, quinone C–H), 2.40 (8H, quartet, J=7.4 Hz, CH_2CH_3), 2.30 (12H, bs, C-3, C-5 CH_3), 1.10 (6H, t, J=7.4 Hz, CH_2CH_3); ($CHCl_3$)/nm 569 (ε 30,000 M^{-1} cm^{-1}); ν_{max} (KBr)/cm^{-1} 3346, 1602, 1560, 1535, 991, 962, 864, 791; *m/z* (FAB) 353 (32), 352 (86), 351 (100, M+H), 350 (79, M) and 349 (42); HRMS calcd for M+H, $C_{22}H_{27}N_2O_2$ 351.2073, found 351.2080. It proved possible to obtain crystals of **5** suitable for X-ray analysis by slow evaporation of a chloroform solution at room temperature.[30]

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